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Adsorption Behaviour of [(4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-(4-methoxy-phenyl)-^{1}methyl]-urea on Stainless Steel in Phosphoric Media

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Abstract

The adsorption of [(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-(4-methoxy-phenyl)-methyl]-urea on iron in phosphoric media was studied by using electrochemical technique. The adsorption mechanism was investigated using adsorption isotherms. The experimental data fit localized adsorption models. The values for free energy of adsorption, ΔG^{o}_{ads} , were also calculated at each surface coverage, θ, of the studied compound by applying the mathematical model of Bockris – Swinkels adsorption isotherm. The variation of free energy of adsorption ΔG^{o}_{ads} with surface coverage, θ, was interpreted in terms of deviation from ideal condition assumed in Langmuir model. A possible adsorption model of HPU2 molecules on to the metal surface was suggested.

Keywords: Corrosion inhibitor, Bockris – Swinkels adsorption isotherm, free energy, stainless steel.

Introduction

The use of inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment is an accepted practice. Corrosion inhibitors are substances which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media. Corrosion protection of inhibitors has been employed to many systems namely, cooling systems, refinery units, chemicals, oil and gas production units, boiler, etc.[1-5].

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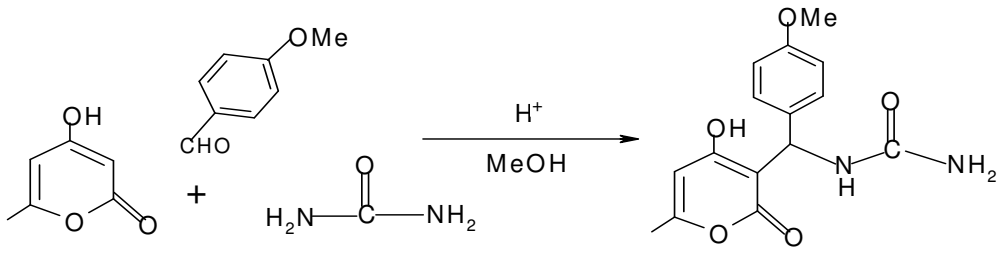
They reduce the corrosion rate by modifying the corrosion potential, retarding the cathodic and anodic corrosion reactions via polarization or passivation of the metal surface. These inhibitors have been found to function by adsorption of their ions or molecules onto metal surface. Hence, accurate elucidation of the mechanism of adsorption of the inhibitor on metal surface is essential for the design and development of new corrosion inhibitors as well as for a detailed understanding of mechanism of the inhibition processes [6-12].

The adsorption of organic molecules on metal surface in electrolytes is often described by adsorption isotherms such as Langmuir, Temkin, Frumkin, Flory-Huggins and thermodynamic – kinetic model, to explain the mechanism of corrosion inhibition on metal surface. However, a glance look at recent literature reveals that there is scarcity of information on the application of Bockris – Swinkels adsorption isotherms to study adsorption of organic compounds on metals. This paper is a continuation of previous work by Chtaini and co-worker on the corrosion behaviour of new class of heterocyclic compounds, two pyrones, [(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-phenyl-methyl]-urea (HPU1) and [(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-(4-methoxy-phenyl)-methyl]-urea (HPU2) on stainless steel in phosphoric media [13]. They found that the two pyrones inhibited the acid corrosion of mild steel and acted as cathodic inhibitors. However, [(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-(4-methoxy-phenyl)-methyl]-urea exhibited higher inhibition efficiency per unit concentration than [(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-phenyl-methyl]-urea. The aim of the present work is to investigate the adsorption of [(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-(4-methoxyphenyl)-methyl]-urea on iron surface according to Bockris – Swinkels adsorption isotherm by using electrochemical method [14].

Material and methods

Synthesis of the new heterocyclic compound

[(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-(4-methoxy-phenyl)-methyl]-urea was prepared from one-pot three-component condensation reaction of 4-hydroxy-6-methyl-2-pyrone, urea and an aromatic aldehyde under acidic condition in methanol (Scheme 1).



[(4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-(4-methoxy-phenyl)-methyl]-urea (HPU 2)

MW = 304.31, $C_{15}H_{16}N_2O_5$

Scheme 1.

The experiments were performed with commercial stainless steel 316 having the chemical composition given in Table 1.

Table 1. Chemical composition (%) of commercial 316 stainless steel.

Specimen	Chemical Composition										
316	C	Si	Mn	Cr	Ni	Mo	Cu	N	P	S	Fe
	0.02	0.50	1.71	16.20	11.00	2.18	0.35	0.07	0.03	0.02	68.06

The measurements were performed in 30% phosphoric acid solution contaminated by Cl^- and SO_4^{2-} ions (30% H_3PO_4 + 330 ppm SO_4^{2-}+1000 ppm Cl^-). The compound ([(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-(4-methoxy-phenyl)-methyl]-urea) was added to acidic media without pretreatment with concentrations of 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4} and 10^{-3} M at 25 °C.

Procedure

The procedure for electrochemical measurement was as described by Bellaouchou et al. [15]. The electrochemical impedance spectroscopy (EIS) measurement was obtained after 30 min of immersion in solution.

Results and discussion

The corrosion rate is expressed in terms of the corrosion current density I_{corr}. Fig. 1 depicts the dependence of the corrosion rate on concentration of HPU 2 in the supporting electrolyte (30% H_3PO_4 + 330 ppm SO_4^{2-} + 1000 ppm Cl^-) at 25 °C. The corrosion rate of the stainless steel in the corrosion media decreases with increasing concentration of the inhibitor in the media. The corrosion rate appears to reach a minimum at concentration 10^{-4} M beyond which the marginal decrease in the corrosion rate is less significant.

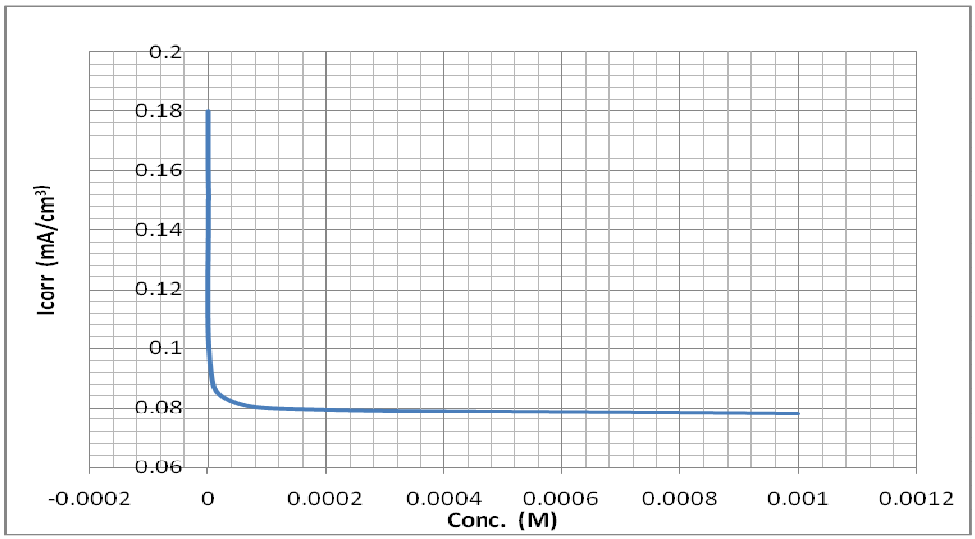


Figure 1. Variation of corrosion rate (mA/cm^2) with concentration of ([(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-(4-methoxy-phenyl)-methyl]-urea) on stainless steel 316 in 30% H_3PO_4 + 330 ppm SO_4^{2-} + 1000 ppm Cl^- at 25 °C.

The corrosion inhibition efficiency (E %) was calculated by:

$$E\% = [(I_{corr} - I'_{corr}) / I_{corr}] \times 100 \quad (1)$$

where I_{corr} and I'_{corr} are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of the cathodic and anodic Tafel lines to corrosion potential (E_{corr}). The surface coverage values θ at electrode (the steel surface) are calculated from the inhibition efficiency as follows:

$$\theta = 1 - I'_{corr} / I_{corr} \quad (2)$$

The variation of the inhibition efficiency with the logarithm of bulk concentration is presented in Fig. 2 for the corrosion media–HPU2 systems at 25^0C. The pattern of the graph in Fig. 2 describes an S – shaped curve. This indicates the formation of a protective barrier film of inhibitor molecules on the steel surface. This agrees with the claim by Chtaini et al. that HPU 2 and HPU 1 act as inhibitors by establishment of a thin film at the metal surface. The film acts as a barrier to the transport of the metal ions from the metal to the solution at high concentration of inhibitor. However, the mechanism of the adsorption process is not yet examined.

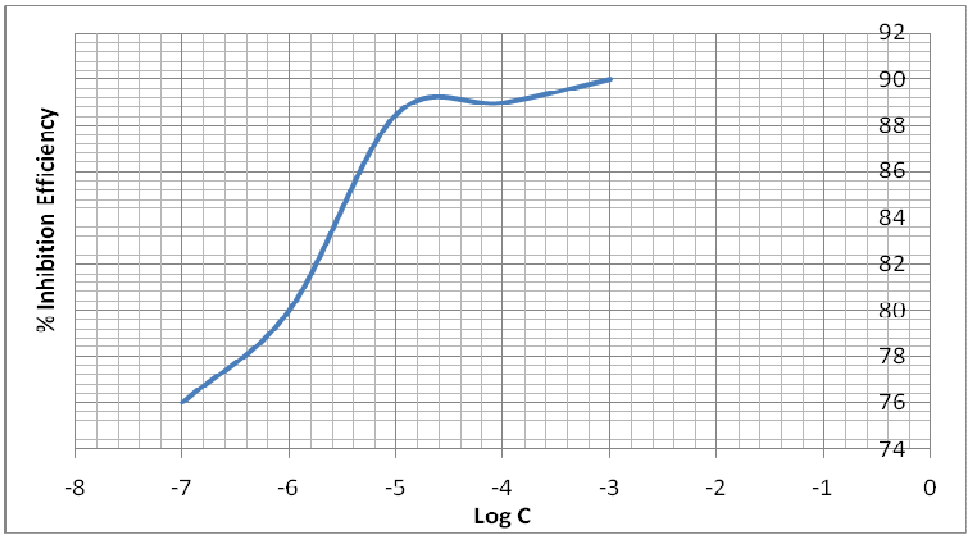


Figure 2. Relationship between inhibition efficiency and concentration of ([(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-(4-methoxy-phenyl)-methyl]-urea) (HPU 2).

Precise elucidation of the mechanism of adsorption of the inhibitor on metal surface is fundamental for the design and evaluation of corrosion inhibitors. Adsorption isotherms are important tools in elucidating the mechanism of surface (organo-electrochemical) reactions. Evaluation with an adsorption isotherm involves an evaluation of its ability to represent raw experimental data, or information derived from such data, after the parameters of the equation have been adjusted to optimize this representation and followed by an evaluation of the physical reasonableness of the optimizing parameters in terms of the physical model on which the equation of state is based [16-19].

Table 2. Parameters of linearization of adsorption models for ([(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-(4-methoxy-phenyl)-methyl]-urea) (HPU 2) adsorption in acidic solutions.

Isotherm	Equation	R^2	ΔG^o_{ads} / J mol^{-1}
Langmuir	$y = 1.11x + 4 \times 10^{-7}$	1	-46449.9765
Volmer	$y = 1.894x + 34.12$	0.909	
Sip/El-Awady	$y = 0.121x + 1.376$	0.879	16486.35963
Flory-Huggins	$y = 8.463x + 12.06$	0.877	16119.77024
Frumkin	$y = 20.06x - 22.76$	0.825	-66340.4168
Hill-De Boer isotherm	$y = -5.015 + 23.92$	0.068	

The results presented in Table 2 show a decrease in the regression coefficient with decreasing simplicity of the model. This clearly suggests that the adsorption mechanism of HPU-2 on stainless steel in the corrosion media agrees with localized surface interaction models with strong adsorbent-adsorbate interaction, very weak lateral interaction between adsorbate molecules and or mobility of adsorbate. Although Langmuir isotherm gave the best fitting of the raw data, its theoretical linearized equation predicts unity as the value of the slope. However, the fitted line gave a value higher than unity for the slope. This suggests a slight deviation from ideal conditions assumed in Langmuir model.

The surface of the electrode in aqueous solution is considered to be covered with water dipoles and for adsorption of organic molecules to occur, these water dipoles must be replaced by organic molecules in a reaction as follows:

$$nH_2O_{\text{electrode}} + \text{Organic}_{\text{solution}} \rightarrow \text{Organic}_{\text{electrode}} + nH_2O_{\text{solution}} \qquad (3)$$

The thermodynamics of the substitution process depends on the numbers of water molecules (n) removed by the organic molecules. The values of the apparent free energy change (ΔG^o_{ads}) for the adsorption process can be evaluated from θ values with Bockris – Swinkels equation which is written as follows [20]:

$$\Delta G^o_{ads} = \left[\frac{55.5\theta}{C_o(1-\theta)^n} \frac{[\theta + (1-\theta)n]^{n-1}}{n^n} \right] \qquad (4)$$

where θ is the surface coverage, n is the number of water molecules being replaced and C_o is the concentration of the organic compound in the bulk solution. Based on a substitutional adsorption process for the space filling models of adsorption of organic molecules on the electrode surface, for $5 \leq n \leq 1$ for adsorption of HPU 2 on the stainless steel surface, the values of ΔG^o_{ads} for the adsorption process were calculated at each θ value obtained using Bocris-Swinkels equation, and are presented in Fig. 3. It is observed that the free energies of adsorption decrease with increasing surface coverage. The same trend is observed in the variation of ΔG^o_{ads} for different n values. The results indicate that there is a slight change in the ΔG^o_{ads} value with change in the n value from 1

to 5. These provide additional evidence of deviation from ideal condition of Langmuir model and suggest steric interactions between the adsorbed molecules on the surface.

On the basis of energetics of the adsorption process two types of adsorption processes have been established: physisorption (electrostatic interaction between the electron density of the molecules and surface atoms of the metal in which the ΔG^{o}_{ads} is up to –20 kJ mol^{-1}) and chemisorption (in which there exist a chemical bond between the molecule or ion and the metal surface where the ΔG^{o}_{ads} is more negative than –40 kJ mol^{-1}) [21-22]. The mean ΔG^{o}_{ads} values of –46.450 kJ mol^{-1} (obtained from Langmuir isotherm) and the range –42. 877 to –46.823 kJ mol^{-1} (calculated from Bockris-Swinkels equation for n = 1,2,..,5) support chemisorption mechanism for the adsorption of HPU2 on the stainless steel surface.

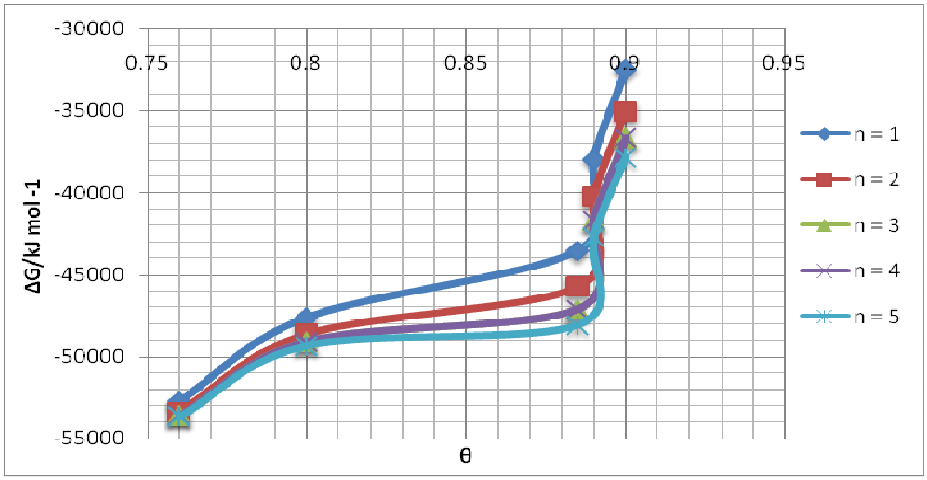
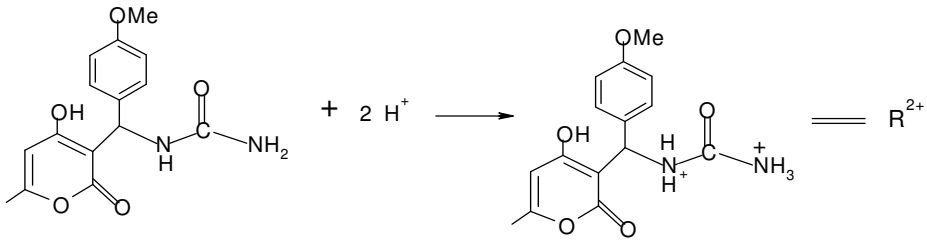


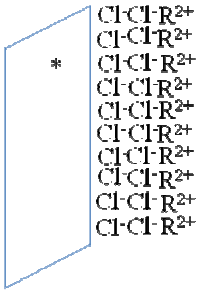
Figure 3. ΔG^{o}_{ads} for ([(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-(4-methoxy-phenyl)-methyl]-urea) (HPU 2) on stainless steel as a function of surface coverage θ in (30% H_3PO_4 + 330 ppm SO_4^{2-} + 1000 ppm Cl^-) as the suporting electrolyte.

It has been demonstrated that anions of acids formed as a result of dissociation of acids influence the mode of adsorption and the degree of inhibition [23]. Molecules of organic compounds containing heteroatoms (O and N) dissolve in acidic solution, to form cations by being protonated at the heteroatoms. The protonation of HPU2 is illustrated in scheme 2:



Scheme 2. The protonation reaction of ([(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl) (4methoxy-phenyl)-methyl]-urea) (HPU 2) in acidic solutions.

These cations are able to adsorb on the metal surface even at high concentration of anions of the acid. The anions (from the electrolyte) on the electrode surface provide a better electrostatic condition, which promotes a direct adsorption of cations on the surface via formation of ion pair [24-25]. The tendency of an anion to form a bridge between the metal and the cations is directly related to its polarisability. The anions of the electrolyte consist of PO_4^{3-}, SO_4^{2-} and Cl^-. Chloride ion is the most polarisable and hence, it is the most relevant of the three for promoting adsorption of the cations (adsorbate). On this basis, adsorption model for HPU2 on the stainless steel surface in the acidic media may be proposed as in model I.



Model I
* The steel surface

Conclusion

- The corrosion rate of the stainless steel in the supporting electrolytes decreases with the increase in adsorbability of HPU2 (values of surface coverage, θ).
- The negative values of ΔG^o_{ads} suggest the spontaneous adsorption of HPU2 on the mild steel.
- The magnitude of ΔG^o_{ads} indicates chemisorption mechanism and HPU2 molecules in cationic form adsorb on the stainless steel surface via formation of ion pair with chloride ion acting as bridge between them.
- The dependence of ΔG^o_{ads} on surface covered, θ is due to deviation from ideal condition assumed in Langmuir model; an indication of steric interaction between adsorbed HPU2 molecules.

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